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Transport and Fate of Organic Pollutants in the Subsurface: Current Perspectives

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TRANSPORT AND FATE OF ORGANIC POLLUTANTS IN THE SUBSURFACE -- Current Perspectives

by

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16. ABSTRACT Protection of ground water from pollution by organic chemicals can only be achieved through proper control and management of source activities which release these substances into the terrestrial subsurface. Control and management procedures must ensure that released organic pollutants are sufficiently attenuated within the subsurface environment to prevent significant impairment of ground water quality at nearby points of withdrawal or discharge, where exposure of humans, animals, and sensitive ecosystems may occur. The only rational basis for technically effective and economical source control and management procedures is definitive knowledge of the transport and fate of organic pollutants in the subsurface, since predictions of the transport and fate of specific organic chemicals in specified subsurface environments will usually be required.

The most effective approaches for predicting subsurface transport and fate of organic pollutants involve the use of mathematical models based on the subsurface processes governing pollutant behavior, which include geohydraulic processes controlling the movement of fluids through porous geological formations, abiotic retarding and transformation processes such as sorption and abiotic degradation and biotransformation processes. Inadequate knowledge of sorption, abiotic transformation, and biotransformation processes in deeper subsurface regions imposes major limitations on current predictive capabilities.

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Transport and Fate of Organic Pollutants in the Subsurface - Current Perspectives

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Abstract

Pollution of ground water by organic chemicals is now recognized as a major environmental problem. Such pollution results from the release of organic chemicals into the terrestrial subsurface by numerous human activities. There is little opportunity for elimination of these source activities or for significantly reducing their magnitude. Therefore, protection of ground water from pollution by organic chemicals must be achieved through proper control and management of these source activities. Control and management procedures must ensure that released organic pollutants are sufficiently attenuated within the subsurface environment to prevent significant impairment of ground water quality at nearby points of withdrawal or discharge, where exposure of humans, animals, and sensitive ecosystems may occur. The only rational basis for developing effective and economical source control and management procedures is definitive knowledge of the transport and fate of organic pollutants in the subsurface. In most cases, predictions of the transport and fate of specific organic chemicals in specified subsurface environments will be required as a basis for estimating the impact of source activities on ground water quality at points of withdrawal or discharge.

The most effective approaches for predicting subsurface transport and fate of organic pollutants involve the use of mathematical models based on the subsurface processes controlling pollutant behavior, which include geo-

hydraulic processes governing the movement of fluids through porous geological formations, abiotic retarding and transformation processes such as sorption and abiotic degradation, and biotransformation processes. Inadequate knowledge of sorption, abiotic transformation, and biotransformation processes in deeper subsurface regions impose major limitations on current predictive capabilities.

Introduction

As long ago as the late 1950's evidence was beginning to emerge which indicated that organic chemicals released into the terrestrial subsurface as the result of various human activities were entering and polluting ground water (Middleton and Walton, 1961). Nevertheless, almost twenty years were to elapse before anyone except a very few scientists and engineers began to consider seriously the possibility that burgeoning production and use of organic chemicals could pose a significant threat to ground-water quality. The primary reasons for this period of neglect included a general lack of knowledge of and interest in ground water on the part of the public and its political entities, preoccupation of most environmental scientists with more readily apparent and immediately pressing problems of air and surface water pollution, and a widely prevailing over-estimation of the protection afforded ground water by the soil mantle. By the mid to late 1970's, however, this indifference and complacency regarding the possible impact of organic chemicals on ground water began to wane. Increasingly frequent reports of gross pollution of ground water by substances such as trichloroethylene, coupled with growing awareness of the potential impact on ground water of hazardous waste disposal activities, at last aroused public concern for this important resource and stimulated scientific scrutiny of ground water for organic contaminants.

Within the past few years, state-of-the-art methodologies for analysis of organic chemicals in aqueous media have been employed with increasing frequency in investigations of ground water pollution incidents and monitoring of ground water quality. Table 1 presents a partial listing, by classes of compounds and numbers in each class, of organic compounds which have been identified in ground waters by such investigations. Although this compilation is not intended to be, and by no means is, all-inclusive, it still includes approximately 200 substances representing a wide range of compositions and structures. Obviously, many organic chemicals have exhibited sufficient mobility and persistence when released into the subsurface under various conditions to adversely impact the quality of ground water. Hence, there now exists little doubt that protection of ground water from pollution by organic chemicals is a major environmental problem which must be successfully addressed if unacceptable degradation of this valuable and irreplacable natural resource is to be prevented. This paper discusses the need for understanding the transport and fate of organic pollutants in the subsurface in addressing this problem, examines approaches in predicting the subsurface transport and fate of organic pollutants, and briefly reviews the current state of knowledge of major subsurface processes which retard the movement or attenuate the concentrations of organic pollutants in subsurface environments.

Protecting Ground Water from Pollution by Organic Chemicals

Numerous human activities can result in the release of organic chemicals into the terrestrial subsurface, where they may enter and pollute ground water. These activities, which comprise the sources of organic pollution of ground water, may be grouped under four major categories.

1. Waste disposal activities which utilize the subsurface as a receptor for organic wastes, such as land treatment of wastewater and land disposal of solid and liquid hazardous wastes.
2. Industrial and commercial operations which accidentally discharge organic chemicals into the subsurface because of spills or leaks occurring during transport, storage, and use of these substances.
3. Agricultural operations involving application of organic chemicals to the land.
4. Artificial recharge of ground water with contaminated water for reclamation and conservation purposes.

Because they are, for the most part, intimately associated with essential functions of industrial society, such source activities are not likely to be eliminated or substantially curtailed in the foreseeable future. The enormous quantities of organic wastes produced by modern industrial societies, coupled with limited opportunities for disposal to other environmental media, indicate that the subsurface must continue to be used as a receptor for many of these wastes. Similarly, the sheer magnitude of current and projected industrial and commercial operations involving organic chemicals makes spills and leaks almost inevitable, in spite of intensive preventive measures. Also, agricultural operations involving application of organic chemicals to the land and artificial

recharge of ground water for reclamation purposes seem destined to be increased or intensified to meet the needs of burgeoning populations. It is obvious, therefore, that protection of ground water from pollution by organic chemicals can only be achieved through proper control and management of these source activities.

Proper source control and management must be effective in preventing unacceptable degradation of ground water quality by organic chemicals and, at the same time, must not entail overly restrictive and expensive regulations which impose an unnecessary economic burden. Hence, efforts to protect ground water from pollution by organic chemicals should properly be directed towards controlling and managing source activities in a manner which ensures that pollutants released to the subsurface will be sufficiently attenuated in concentration within this environment to prevent significant impairment of ground water quality at nearby points of withdrawal or discharge. This approach emphasizes the need to protect the quality of ground water at points of withdrawal or discharge, where humans, animals, and sensitive ecosystems may be exposed to harmful concentrations of organic pollutants. The necessity for utilizing the subsurface as a pollutant receptor is recognized, and proper consideration is afforded the fact that source control and management efforts must make maximum practicable use of the capacity of the subsurface for attenuating concentrations of organic pollutants if they are to be cost effective. Also inherent in this approach is recognition that, although there will be situations where no entry of organic pollutants into ground water can be tolerated, the movement of these substances into the deeper unsaturated zone and even into ground water may be acceptable at many sites of source activities where the attenuative capacity of the subsurface is sufficient to ensure that unacceptable concentrations will not reach nearby points of ground-water withdrawal or discharge.

In practical terms, effective source control and management actually involves the attainment of four principal goals. First, new source activities (e.g. wastewater and hazardous waste land disposal operations and artificial recharge activities) must be located, designed, and operated in a manner which ensures that organic pollutants released into the subsurface will not adversely affect groundwater quality at nearby points of withdrawal or discharge, while still making maximum safe use of the subsurface as a pollutant receptor. Second, the potential impact of existing sources (e.g. active or closed hazardous waste disposal sites and locations of accidental discharges) on ground water at nearby points of withdrawl or discharge must be accurately assessed as the basis for remedial actions which effectively achieve the desired level of protection of ground water quality without being more complex and costly than needed. Third, new organic chemicals with the potential for excessive impact on ground water quality when released into the subsurface through various source activities must be identified prior to manufacture as the basis for implementation of restrictions on production, use, and/or disposal of these substances needed to prevent or minimize their entry into ground water. Finally, improved methods for eliminating organic pollutants from the subsurface must be developed in order that existing sources can be more efficiently controlled and managed and the subsurface may be more effectively used as a pollutant receptor.

Obviously, attainment of these goals requires an understanding of the transport and fate of organic pollutants in both unsaturated and saturated subsurface regions. Indeed, in most cases the capability to predict the transport and fate of specific organic pollutants in particular subsurface environments will be required as the basis for estimating the impact of various source activities on ground water quality at nearby points of withdrawal or discharge.

Definitive information concerning the transport and fate of organic pollutants in the subsurface is the key to controlling and managing the sources of organic pollution of ground water in a manner that is effective from both the technical and economic viewpoints. If efforts to protect ground water from pollution by organic chemicals are not based on such information, the result will almost certainly be either under control, with excessive degradation of ground water quality, or over control, with uneconomical under-utilization of the subsurface as a pollutant receptor.

Predicting Transport and Fate of Organic Pollutants in the Subsurface

Much of the relatively limited scientific effort concerning pollution of ground water by organic chemicals has been devoted to monitoring the occurrence and concentrations of pollutants in ground water at points of known or suspected pollution. The information gained in these field monitoring studies can provide limited insights regarding the subsurface transport and fate of those particular compounds which have been identified in the monitored ground waters.

In the case of one group of compounds, the chlorinated methanes, ethanes, and ethenes, enough field monitoring data have been accumulated to permit conclusions concerning subsurface transport and fate of these substances that are sufficiently general to be useful in estimating source impacts on ground water quality. These compounds have been identified as ground water pollutants in numerous monitoring studies at widely varying locations. This is illustrated by Table 2, which presents partial results obtained when ground water from 670 wells in New Jersey and 232 pumping stations in the Netherlands were monitored for volatile organic pollutants (Tucker, 1981; Zoeteman et al.,

1981). In both studies the same five compounds - trichloromethane, tetrachloromethane, trichloroethene, tetrachloroethene, and 1,1,1-trichloroethane - were detected most frequently. Frequencies of occurrence ranged from 15 to 27 percent of wells sampled in New Jersey and from 17 to 67 percent of pumping stations sampled in the Netherlands. The widespread and frequent occurrence of these compounds in ground water at many different locations leaves little doubt that they are highly mobile and very persistent in many subsurface environments, and indicates that their release in appreciable quantities into the subsurface through any source activity is likely to result in an undesirable impact on ground-water quality at nearby points of withdrawal or discharge.

In most cases, however, field monitoring data are far too limited to permit such generalizations. Little rationale exists for extrapolation of monitoring data concerning the behavior of a specific organic pollutant in a particular subsurface environment to predict the transport and fate of this compond at other sites or of other compounds at the same site. Also, monitoring data usually provide no basis for the quantitative predictions of pollutant transport and fate which are often needed in source control and management decisions. Hence, transport and fate predictions based on field monitoring data must usually be very subjective qualitative estimates which serve a useful purpose in source control and management efforts only during preliminary problem evaluation or when no other approach to predicting pollutant transport and fate is practicable.

Microcosms (physical models) can provide a useful approach in predicting the transport and fate of organic pollutants in specific subsurface environments. In this approach, microcosms are constructed and operated to simulate a portion of a natural subsurface system as closely as possible. The transport and fate

of the organic chemicals of interest are then evaluated in the microcosms, with chemicals being applied in a manner that simulates release by a specific source. The data obtained are used to predict the transport and fate of the evaluated chemicals in the parent subsurface system.

An example of the use of microcosms for predicting the subsurface transport and fate of an organic chemical is found in work of the U.S. Environmental Protection Agency pertaining to nitrilotriacetic acid (NTA) (Dunlap et al., 1972). The objective of this work was to provide an estimate of the impact on groundwater quality which would occur if polyphosphate builders in detergents were replaced by NTA. Soil column microcosms were used to simulate unsaturated soil profiles under septic system lateral lines operating as designed, without significant flooding, and saturated soil profiles under improperly operating (flooded) laterals or wastewater lagoons. Simulated aquifer microcosms constructed from authentic aquifer material were employed to mimic saturated ground water environments lying beneath the water table. After approximately six months of operation the data obtained from these systems permitted the following conclusions.

1. NTA released into unsaturated profiles of the tested soils by properly operating laterals would have no impact on ground water, since it would be degraded during passage through one meter of such soil.
2. NTA released into saturated profiles of the tested soils by improperly operating laterals or wastewater lagoons would persist in the saturated soil and enter ground water with little attenuation.
3. NTA would be likely to move readily through aquifer material of the type tested, but concentrations would be reduced by anaerobic degradation.

If this study had incorporated relatively small improvements in experimental

design and data interpretation, predictions concerning the subsurface transport and fate of NTA which were more quantitative in nature would have resulted. Nevertheless, the information obtained was quite valuable to contemporary ground water protection efforts, and the work illustrates the utility of microcosms for predicting transport and fate of organic chemicals in subsurface environments.

The use of microcosms for predicting subsurface transport and fate does, however, have inherent limitations which diminish the overall utility of this approach. First, it is empirical in nature; hence, there is little rational basis for extrapolation of information obtained to other compounds and other subsurface environments. Second, the construction and operation of microcosms is usually very costly and time consuming, so it is entirely infeasible that microcosms can be employed to evaluate the subsurface transport and fate of all of the thousands of organic chemicals which may be released into the subsurface by different source activities in all of the different environmental situations which they may encounter. Microcosms are extremely useful tools for investigating the processes which affect organic pollutants in the subsurface and for testing of mathematical models of subsurface systems (Wilson et al., 1981; Wilson et al., 1983b; Suflita and Miller, 1984). They will probably continue to find use for predicting transport and fate of specific organic pollutants or wastes in particular subsurface environments. However, it is apparent that a more systematic approach to prediciting subsurface transport and fate of organic pollutants is required to provide the basis for effective and economical control and management of sources of organic pollution of ground water.

The most systematic and potentially effective approaches to predicting the transport and fate of organic pollutants in the subsurface are based on understanding the processes which control the behavior of organic chemicals in sub-

surface environments. These processes include: geohydraulic processes that pertain to the movement of fluids through porous geological formations comprising the framework of subsurface environments; abiotic processes which retard the movement or attenuate the quantity of chemicals, such as sorption or abiotic transformation; and, biological processes which primarily decrease the quantity of pollutants through biotransformation or biodegradation. Mathematical descriptions of these processes may be incorporated into mathematical systems models which integrate subsurface process descriptions with environmental (site) characteristics and pollutant properties to yield quantitative estimates of pollutant concentrations in the subsurface on a temporal or spatial basis. Such information is, of course, what is needed for effective control and management of the sources of organic pollution of ground water.

A number of mathematical models with some degree of utility for predicting the subsurface transport and fate of organic pollutants in subsurface environments have been developed in recent years. These models vary quite significantly in their complexity, applicability, and input requirements. The major limitations on their performance are inadequacies of the process descriptions on which they are based and difficulties in obtaining input parameters required by these process descriptions, or sub-models. The less empirical the process descriptions or, conversely, the better their theoretical basis, the more widely applicable and effective the systems model will be.

Because the quantitative aspects of ground-water resource management have long been of interest, the geohydraulic processes have been the object of investigation for many years. Hence, currently available systems models are most robust in regard to geohydraulic process descriptions. On the other hand, the abiotic and biological processes which retard the movement and decrease the concentration of organic pollutants in the subsurface have received relatively

little attention, and descriptions of these processes are generally the weakest links in current systems models. Important questions remain to be answered concerning the geohydraulic processes, particularly those pertaining to dispersion, spatial variability, and flow of immiscible fluids. However, the greatest current need for successful prediction of the subsurface transport and fate of organic pollutants is for delineation and quantitation of the subsurface abiotic and biological retarding and attenuating processes, including sorption and abiotic and biological transformation or degradation. It is, therefore, worthwhile to very briefly review the current state of knowledge concerning these subsurface processes.

Abiotic Processes

Sorption

Sorption of organic chemicals on the solids comprising the subsurface matrix can have a profound effect on their rate of travel both through the unsaturated zone into ground water and the saturated zone to points of ground water withdrawal or discharge.

Primarily because of concern for the environmental fate of pesticides, considerable information pertaining to the sorption of organic chemicals to surface soils and aquatic sediments has been developed over the past 20 years. This information provides insights useful in attempting to predict transport of organic pollutants into and through ground water, although it must be used with care because solids from the deeper subsurface below the root zone may differ significantly from surface solids and sediments, particularly in organic carbon content.

Work with surface soils and aquatic sediments has revealed that sorption of organic chemicals by these materials can generally be described by the Freundlich

equation or sorption isotherm, presented below.

$$\frac{x}{m} = KC^{1/n}$$

where $\frac{x}{m}$ = mass of organic compound sorbed per unit mass of subsurface solids

C = concentrations of organic compound in the pore water

K & n = empirical constants

In the case of neutral, hydrophobic organic compounds of very low polarity - a classification which includes many compounds of environmental concern - the quantity of compound sorbed has been observed to be directly proportional to the concentration in solution over a wide range of concentrations. This apparently occurs because sorption results almost entirely from interaction between the immobile native organic matter of the soil and the solute molecules, with the immobile organic matter acting essentially as a hydrophobic solvent into which the solute molecules are partitioned (Chiou et al., 1979). When sorption occurs by this mechanism, termed hydrophobic sorption, the Freundlich n term becomes unity and K becomes, in effect, a partition coefficient or distribution coefficient. The retardation of travel of a particular chemical relative to the movement of water through a specified soil can then be estimated from K, the distribution coefficient for that compound - soil system, by means of the following equation (Hashimoto et al. 1964).

$$R = 1 + \frac{\rho}{\theta} K$$

where R = retardation of movement of the organic compound relative to water movement

ρ = bulk density of the soil (g soil/cm^3 soil)

θ = volumetric water content of the soil (cm^3 water/cm^3 soil)

K = distribution coefficient

The coefficient of distribution for a specific chemical in a particular soil system can be obtained from batch sorption tests in which the distribution of the compound between the aqueous and solid phase is determined experimentally in the laboratory. Such tests are, however, time consuming and relatively expensive. Hence, considerable effort has been devoted in recent years to the development of methods which minimize or eliminate the necessity for laboratory sorption tests to obtain K values for compounds undergoing hydrophobic sorption. The basis for these efforts was provided by the observation that, for many organic compounds, when the coefficients of distribution obtained for the same compound in several soils were normalized for the organic carbon contents of the soils, essentially the same values were obtained for all the test soils (Goring, 1962). This has led to the development of the following relationship based on soil organic carbon content.

$$K_{OC} = K/F_{OC}$$

where K_{OC} = soil solids - soil water distribution coefficient normalized to soil organic carbon content

K = soil solids - soil water distribution coefficient

F_{OC} = fraction of dry weight of soil that is organic carbon

The above relationship indicates that, assuming all soil organic matter behaves in the same way in hydrophobic sorption, K_{OC} is a property only of the organic compound and is independent of soil properties. Hence, once K_{OC} is obtained for a compound by experimental sorption tests with one soil, the distribution coefficient, K, for this compound in any other soil can be estimated simply by multiplying the fraction organic carbon, F_{OC}, of that soil by the K_{OC} for the compound.

Since K_{OC} is a function only of the sorbed organic compound, it should theoretically be possible to predict this value for a given compound from other,

more readily obtainable, properties of the molecule, thus obviating the need for any laboratory sorption tests. In actual fact, a number of empirical relationships have been developed which relate K_{OC} to either solubility or octanol-water partition coefficient, K_{OW}. These relationships, which have been developed by regression analyses of experimental sorption data for a number of different classes or groupings of organic compounds in various soils, take the following general form.

$$\log K_{OC} = A \log X + B$$

Where X = solubility or K_{OW}

A & B = empirical regression constants

For example, Kenaga and Goring (1980) have developed the following equation relating solubility and K_{OC} from data for 170 compounds, primarily pesticides.

$$\log K_{OC} = 3.64 - 0.55 \log S$$

Where S = solubility in mg/l

A similar equation relating K_{OW} and K_{OC} has been derived by Karickhoff et al. (1979) from data for a group of aromatic and chlorinated hydrocarbons.

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21$$

Other equations relating solubility and K_{OC} have been developed by Chiou et al. (1979) and Briggs (1981), while Brown and Flagg (1981), Briggs (1981), Griffin et al. (1980), Kenaga and Goring (1980), Mabey et al. (1981), Means et al. (1980), and Schwartzenbach and Westall (1981) have derived additional equations relating K_{OW} and K_{OC}.

Under optimum conditions, reasonably good estimates of K_{OC} can be obtained from data for solubility or K_{OW} by means of the above relationship. For example, Kenaga (1980) reported that values for K_{OC} predicted from solubilities by the equation of Kenaga and Goring (1980, presented above) were within one order of magnitude of experimental values for 96 of 110 compounds studied.

However, predicted values also may sometimes be seriously in error. This is particularly likely to occur if predictions of K_{OC} are attempted for compounds which differ significantly in structure and properties from those employed for derivation of the regression equation used. Therefore considerable caution must be exercised in making such predictions.

Based on the above relationships, it is possible to estimate the extent to which sorption will retard the movement, relative to the movement of water, of a neutral, hydrophobic organic compound released into a subsurface environment if the solubility or K_{OW} of the compound and the fraction organic carbon (F_{OC}), bulk density (ρ), and volumetric water content (θ) of the subsurface solids are known. This involves three steps.

1. Using an appropriate regression equation, calculate K_{OC} for the compound from S or K_{OW}.
2. Obtain the coefficient of distribution, K, from $K = K_{OC}F_{OC}$.
3. Calculate the retardation constant , R, from $R = 1 + \frac{\rho}{\theta} K$.

In attempting to use this procedure, it must be remembered that the entire approach is based on the premise that sorption results almost entirely from interactions of organic solute with immobile native organic matter in the subsurface solids (hydrophobic sorption). In reality, however, sorption of all but the most non-polar, hydrophobic neutral organic compounds is likely to involve other interactions, probably occurring through a combination of competing interactions with clays and hydrous oxides, as well as native organic matter. Hence, utilization of this approach for predicting sorption and retardation of movement of any organic compounds except those which are highly non-polar and hydrophobic would appear questionable.

In addition, there is yet another pitfall in attempting to predict sorption of organic pollutants in the subsurface on the assumption that hydrophobic sorption is the only sorptive process of importance. This results from the fact that the major part of the subsurface that organic pollutants must ordinarily traverse in moving from source activities to points of ground water withdrawl or discharge is comprised of geological solids lying below the root zone. The fraction of native organic matter present in these deeper-lying materials will usually be very low, in which case sorption, even of very hydrophobic compounds, is likely to be dominated by inorganic components of the solid matrix (McCarty et al., 1981; Schwartzenbach and Westall, 1981). Hence if sorption is predicted entirely on the basis of the organic carbon content of this material it may be significantly underestimated.

Clearly, progress has been made in understanding the sorption of organic chemicals by subsurface solids, but much additional information is needed for developing a comprehensive capability for predicting the transport of organic pollutants in all subsurface environments. In particular, research is needed to better define the critical parameters impacting sorption of organic compounds in the deeper subsurface regions, where organic carbon is apt to be very low, and to elucidate and quantify the mechanisms of sorption of compounds of a more polar character. In addition, the kinetics of sorption/desorption need to be explored more thoroughly to determine the validity of treating sorption as an equilibrium process in subsurface systems models, and sorption of organic pollutants from mixed solvent systems such as may occur near hazardous waste disposal sites should be investigated.

Abiotic Transformation

Abiotic transformation processes have probably received less attention than any of the processes which are likely to affect organic pollutants in the subsurface. Nevertheless, both logic and limited experimental observation would seem to indicate a very significant potential for abiotic transformation of organic chemicals in subsurface environments, primarily because of possible reactive and/or catalytic properties associated with the large surface areas of subsurface solids matrices, and also because of the presence in some ground waters of reactive inorganic solutes such as HS^- and Fe^{++}.

Research pertaining to the reactions affecting the activity of pesticides in agricultural soils has provided limited insights regarding solids-related abiotic transformations. Such work has demonstrated that abiotic transformation of organic compounds can be mediated by the native organic matter of the soil matrix. Although soil organic matter contains many reactive nucleophilic groups as well as free radicals which could conceivably lead to a wide variety of abiotic transformations of influent organic solutes, the transformations that have been demonstrated are primarily hydrolytic in nature. For example, soil organic matter has been shown to catalyze the hydrolysis of S-triazine pesticides, resulting in displacement of ring chlorine substituents by hydroxyl groups (Armstrong and Chesters, 1968; Nearpass, 1972), and of organophosphate pesticides, resulting in cleavage of ester linkages (Armstrong and Konrad, 1974). Pesticide research has also provided evidence for mediation of abiotic transformations of organic chemicals by clay minerals. This is illustrated by investigations of Mortland (1970) in which metal ion-clay complexes were observed to catalyze decomposition of both organophosphate and S-triazine pesticides.

Abiotic transformation of organic pollutants in the saturated subsurface through reactions with reactive inorganic solutes present in ground water has been demonstrated by Giger and Schaffner (1981) and Schwarzenbach and Giger (1981). In these studies alkyl bromides released into the subsurface at the site of an abandoned chemical plant were shown to have been converted to dialkylsulfides and cyclic disulfides through reactions with hydrogen sulfide present in the anaerobic ground water.

From the above, it is obvious that currently available information concerning abiotic transformation of organic chemicals in the subsurface is extremely limited. This information is sufficient, however, to indicate strongly that abiotic transformation processes are likely to have a significant impact on the fate of at least some organic pollutants in specific subsurface environments. This is especially true in view of the fact that detention times of organic pollutants in subsurface environments will often be sufficiently long to allow even very slow reactions to proceed far toward completion. Hence, there is need for a strong research effort to elucidate and quantify abiotic transformation processes affecting organic chemicals in the subsurface.

Biological Processes

The role of microorganisms in destroying organic pollutants in surface waters and the topmost soil layers has long been appreciated, but only very recently has it been recognized that biotransformation or biodegradation of organic chemicals in those regions of the subsurface lying below the root zone may be of fundamental importance in controlling the quality of ground water. This situation arose primarily because of a long-standing assumption among most microbiologists that the deeper regions of the subsurface were essentially devoid of life. The basis of this assumption was information developed by

early soil microbiologists, using plate counting procedures employing nutrient agar or similar growth media, which seemed to indicate that numbers of microorganisms decreased rapidly with soil depth (Waksman, 1916). However, recent studies employing new techniques which permit enumeration of all living organisms in soils and underlying subsurface solids, rather than just those that can grow on a particular growth media, have clearly shown the presence of very significant populations of microorganisms in both unsaturated and saturated subsurface environments lying below the root zone.

Densities of microorganisms found in subsurface samples obtained from several shallow water table aquifers and associated unsaturated formations are presented in Table 3. These samples were obtained by special drilling and coring procedures which essentially precluded contamination by surface microbes, and microorganisms were enumerated by a modified epifluorescence microscopy technique (Wilson et al., 1983a; Ghiorsi and Balkwill, 1983). As shown by Table 3, the numbers of microorganisms detected in all of the subsurface samples examined were surprisingly high, falling mostly in the range of 10^6-10^7 cells per gram of dry material. These values are comparable to microbial densities occurring in eutrophic surface waters. In addition, the numbers of microorganisms did not decline significantly with depth, and there was surprisingly close agreement in numbers found in cores obtained at the same site at different times of the year and in cores obtained from replicate bore holes.

Microcosms constructed from some of the subsurface materials used in the above enumeration studies were also employed for studies to determine if the subsurface microbes indigenous to these materials were capable of transforming organic pollutants of environmental concern (Wilson et al., 1983b). Table 4 presents results obtained when these microcosms were dosed with a group of

selected organic chemicals and the systems were operated for a period of 16 weeks. As these data show, most of the subsurface materials which were studied contained microorganisms which transformed chlorobenzene, toluene, and styrene, but none contained organisms which appeared to be active toward chlorinated methanes, ethanes, and ethenes. It should be noted, however, that the latter compounds are apparently biotransformed, at least at a significant rate, only in deeply anaerobic environments (Bouwer et al., 1981), while the microcosms used in this work were operated under essentially aerobic conditions.

Additional evidence that microorganisms indigenous to the deeper subsurface are capable of transforming organic pollutants is found in the results of other recent laboratory and field studies pertaining to ground water pollution. For example, Roberts et al. (1982) reported evidence for long term biotransformation of chlorinated hydrocarbons in an aquifer at an artificial recharge site in California, while Suflita and Miller (1984) observed the biotransformation of chlorophenols in microcosms constructed from authentic subsurface material obtained from an aquifer in Oklahoma. Also, Ehrlich et al. (1982) observed biodegradation of phenolic compounds in an aquifer at the site of a former wood creosoting plant in Minnesota, and Wilson et al. (1984) reported biotransformation of polyaromatic hydrocarbons of relatively low molecular weight in an aquifer at a similar site in Texas.

In its totality, the information presented above leaves little doubt that many organic chemicals are very likely to undergo biotransformation in the deeper regions of the subsurface. The rate and extent of such transformation or degradation in a specific subsurface environment will depend on the geochemical properties of the environment, the microbial populations present in the environment, and the nature and quantity of the pollutants.

The geochemical properties of a subsurface environment are likely to impose constraints on the extent of biodegradation that can occur in that environment. In particular, available supplies of nutrients such as nitrogen and phosphorus, and electron acceptors, primarily oxygen, may become limiting. It may be possible to use the quantities of these substances that are present in a subsurface region to estimate an upper boundary for the quantity of organic pollutant that can be biodegraded in that region. For example, normal ground waters often contain 0.1 to 10 mg/l of nitrate, which is equivalent to approximately 0.02 to 2.2 mg/l nitrogen. Since bacteria are about 15% nitrogen on a dry weight basis, approximately 0.15 to 15 mg/l of cell mass could be produced from the available nitrogen. Assuming an efficiency of incorporation of 50%, then 0.3 to 30 mg/l of organic compound could be degraded before nitrogen becomes limiting.

Such calculations are obviously crude, but are useful in providing at least some indication of the constraints imposed on biodegradation by geochemical factors. Based on such considerations, as well as limited field observations, Wilson and McNabb (1983c) have postulated that biodegradation of 1-10 mg/l of organic pollutant is likely to completely deplete oxygen and/or other metabolic requirements in most ground waters.

While the extent of biodegradation of an organic pollutant in a specific subsurface environment is likely to be limited by the geochemical properties of that environment, the rate of biodegradation will be limited by the numbers and activities of the microorganisms present in the environment, as well as the nature and quantity of the pollutant itself. Obviously, the pollutant will be biodegraded only if microorganisms that are capable of metabolizing it are present in the environment. If biodegradation of the pollutant occurs when it is introduced into the subsurface environment in very low concentration, it

will almost certainly be only one of a number of organic substrates contributing to the metabolic requirements of the indigenous microbial population. The rate of biodegradation will be proportional to the concentration of the pollutant, and will be low. If the concentration is increased, the rate of biodegradation will also increase, but will remain proportional to pollutant concentration until a threshold concentration is reached where the pollutant makes an ecologically significant contribution to the metabolism of those microbes which use it, providing them with a competitive advantage over those organisms which do not. When this occurs, the relative proportion of microbes degrading the pollutant will increase, resulting in adaptation of the microbial population to the pollutant and a dramatic increase in the rate of its degradation.

These subsurface biodegradation scenarios can be described by a computer simulation, shown in Figure 1, that portrays the effect of concentration of a pollutant on its biodegradation in a subsurface environment initially containing a low density (10^3/g) of active microorganisms. This simulation predicts that degradatin of pollutant will be first order at concentrations of 10 µg/l or lower, with no adaptation occurring until concentrations approach 100 µg/l. Available information indicates that these predictions may correspond reasonably well with the actual behavior of natural systems.

The adaptation or lack of adaptation of the microorganisms in a specific subsurface environment to an influent organic pollutant will be of major importance in predicting the biodegradation of the pollutant in that environment (Wilson et al., 1984). If adaptation does not occur, biodegradation of the pollutant will be determined by the rate of its utilization by the microbial community indigenous to the environment. Quantitative predictions of biodegradation will require delineation and description of the kinetics of the utilization (biodegradation)

processes. On the other hand, if adaptation does occur, the rate of biodegradation of the pollutant will become so rapid as to be considered instantaneous within the context of slow ground water movement. Quantitative prediction of biodegradation must then be based on the extent of utilization of the compound allowed by geochemical constraints on microbial metabolism and the rate of replenishment of the limiting requisites for metabolism to the subsurface environment.

In spite of recent advances, current knowledge remains very meager concerning the densities and types of microorganisms present in deeper subsurface environments, the types of organic compounds that they can metabolize, and their principal metabolic pathways. Hence, the kinetics of biodegradation of specific organic chemicals in particular subsurface environments must usually be determined experimentally, employing microcosms constructed from authentic subsurface solids material obtained from the site of interest. Similar, relatively complex experimental procedures must also be employed to determine if microorganisms in a subsurface environment of interest have adapted to, or are likely to adapt to, a specific organic pollutant. However, as research pertaining to the subsurface biodegradation of organic pollutants continues to provide additional information concerning the distribution, composition, and metabolic capabilities of subsurface microbial populations, the need for relatively extensive site and pollutant specific experimentation in order to project the course of biodegradation of a specific organic pollutant in a particular subsurface environment should be greatly reduced.

NOTICE

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication.

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Table 1. Partial Listing by Classes of Organic Compounds Detected in Ground Water

Class	Number per Class
Aliphatic Hydrocarbons	24
Halogenated Aliphatic Hydrocarbons	28
Aromatic Hydrocarbons	27
Halogenated Aromatic Hydrocarbons	6
Phenols	10
Halogenated Phenols	5
Other Halogen-Containing Compounds	17
Other Oxygen-Containing Compounds	53
Compounds Containing Nitrogen and/or Sulfur	27
Compounds Containing Phosphorus	3

Table 2. Frequency of Detection of Halogenated Methanes, Ethenes, and Ethanes in Ground Water

Compound	New Jersey (670 Wells)(1)		The Netherlands (232 Pumping Stations)(2)
	% Samples >M.R.C.	Minimum Reportable Concentration (M.R.C.) µg/l	% >0.01µg/l
Carbon Tetrachloride (Tetrachloromethane)	27	0.1	43
Trichloroethylene (Trichloroethene, TCE)	26	0.3	67
Tetrachloroethylene (Tetrachloroethene, PCE)	23	0.1	19
1,1,1-Trichloroethane (Methyl Chloroform)	21	2.0	17
Chloroform (Trichloromethane)	15	0.8	60

(1) Tucker, 1981.
(2) Zoeteman, DeGreef, and Brinkmann, 1981.

Table 3. Density of Microorganisms in Subsurface Environments

Site	Depth to Water Table (M)	Millions Per g Dry Material		
		Subsoil	Above Water Table	Below Water Table
Lula, OK (1)	3.6			
February 81		6.8	3.4	6.8
June 81		9.8	3.7	3.4
Fort Polk, LA (2)				
Borehole 6B	6.0	3.4	1.3	3.0
Borehole 7	5.0	7.0	1.3	9.8
Pickett, OK (2)	5.0	nd	nd	5.2
Conroe, TX (3)	6.0	3.3	6.0	2.1
Long Island, NY (3)	6.0	nd	nd	36
	3.0	40	nd	nd

(1) Wilson et al., 1983a.
(2) Ghiorsi and Balkwill, 1983.
(3) W.G. Ghiorsi (personal communication, 1983)

nd = no data.

Table 4. Degradation of Organic Pollutants in Subsurface Core Materials (1,2)

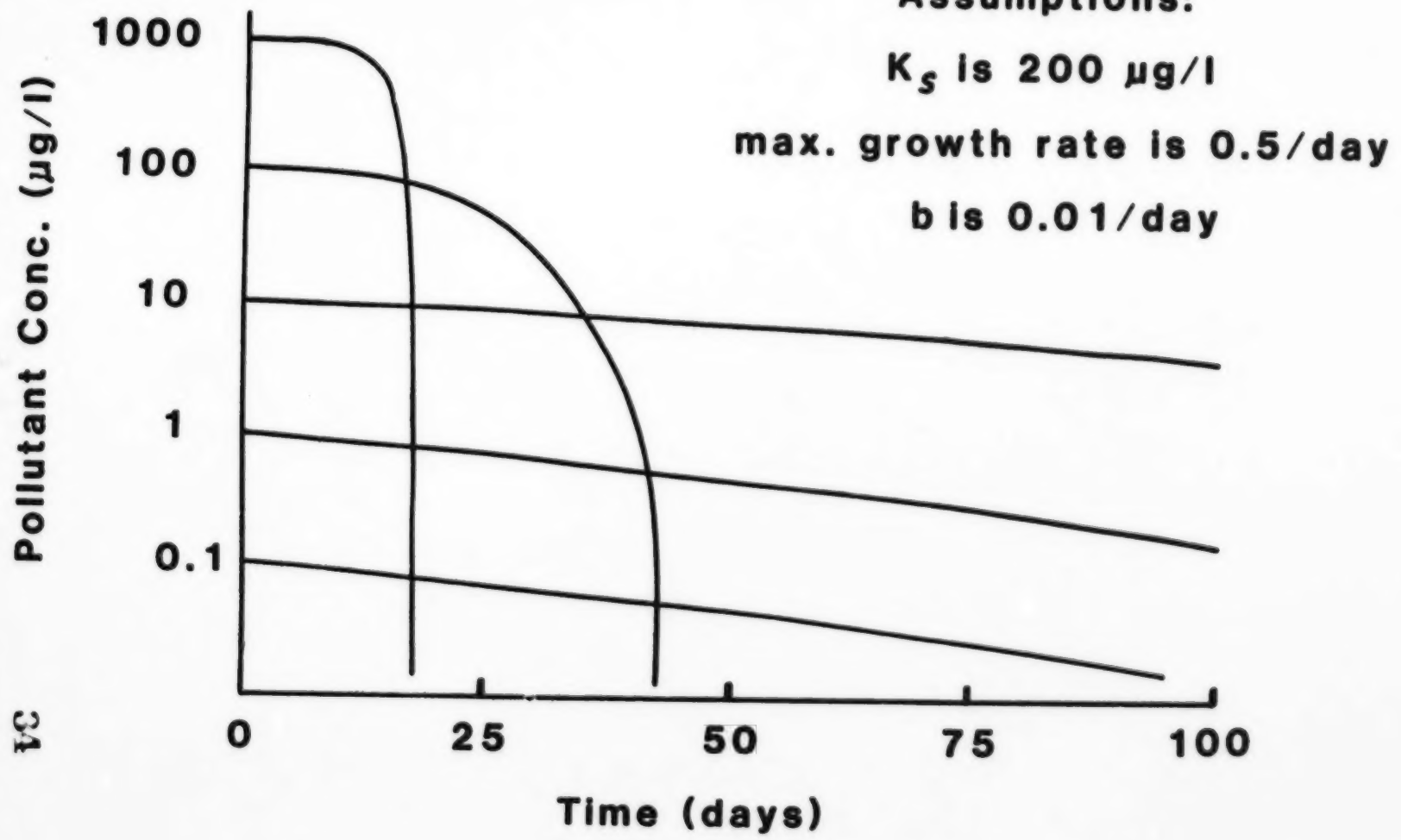
Compound	Lula, OK (Clay)		Fort Polk, LA (Loam)		Pickett, OK (Sand)	
	Above(3)	Below(3)	Above(3)	Below(3)	Above(3)	Below(3)
Trichloroethylene	S	S	S	S	S	S
Tetrachloroethylene	S	S	S	S	S	S
1,1,1-Trichloroethane	-	-	S	S	S	S
Chloroform	-	-	S	S	S	S
1,2-Dichloroethane	S	S	-	-	-	-
Chlorobenzene	D	S	S	S	D	D
Toluene	D	D	D	D	D	D
Styrene	-	-	D	D	D	D

(1) Wilson et al., 1983a.
(2) Wilson et al., 1983b.
(3) Samples taken immediately above and below the water table.

S = Stable
D = Degrades

LEGEND FOR FIGURE

Figure 1. Computer simulation of the effect of the concentration of an organic pollutant on its biodegradation.


Assumptions:
K_s is 200 µg/l
max. growth rate is 0.5/day
b is 0.01/day
Pollutant Conc. (µg/l)
1000
100
10
1
0.1
0
25
50
75
100
Time (days)